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Abstract

Representative, simplified geothermal rock – fluid systems are investigated with a modeling approach to estimate how rock water interactions affect coupled properties related to mechanical stability and permeability improvement through fracturing. First, geochemical modeling is used to determine the evolution of fluid chemistry at temperatures up to 300 °C when fluids are in contact with representative rocks of continental origin. Then, a kinetic crack growth model for quartz is used to predict growth rate for subcritical cracks in acidic and basic environments. The predicted growth rate is highly sensitive to temperature and pH in the ranges tested. At present, the model is limited to situations in which quartz controls the mechanical process of interest, such as well bore stability in silica cemented rocks and the opening of quartz filled veins to enhance permeability.

Introduction

Geothermal reservoirs are highly reactive geochemical environments. Laboratory studies of fracture growth in rocks and minerals at low stress indicate that failure and related processes depend on chemical effects at crack tips. In this study, we show how geochemical modeling can be used to simulate the active chemical environment that exists in contact with a simplified reservoir rock at reservoir temperature. We then use the geochemical simulator to predict the changes in the chemical environment that result from a well-bore chemical treatment. The computed fluid chemistry is then used as input to estimate the effect of the chemical treatment on the mechanical integrity of the reservoir, based on a laboratory-derived constitutive model relating pH and subcritical crack growth rate. We demonstrate our approach using a constitutive model for quartz. Although the crack growth model applies only to quartz, quartz is important in geothermal systems. For example, quartz veins are nearly ubiquitous in geothermal reservoirs, and are often associated with fracture permeability and zones of mechanical weakness.

Preliminary modeling is limited to simple systems in this study in order to identify general effects and to broadly evaluate the importance of rock water interactions on mechanical properties. Mechanical stability, fracturing and related properties are important in several practical situations. The viability of a geothermal reservoir is often limited by fracture permeability. Engineering favorable fractures or enhancing the tendency of the formation to fail appropriately is an attractive long-term goal. For example, hydrofractures typically propagate parallel to the natural fracture system defined by the tectonic stress field. The resulting connectivity between induced fractures and the natural fracture system is often inadequate to significantly improve permeability and heat transfer. One possible means for altering fractures *in-situ* might be to use rock water interactions to modify hydrofracturing with chemical pretreatments. Geochemical effects may also influence how fractures grow and propagate when

driven by the ambient tectonic and thermal stresses naturally present in a reservoir, and may be important contributors to breakouts, borehole failures, and lost circulation. The susceptibility of a mineral surface to fracture is a balance between dissolution (surface bond breakage) (Dove, 1995), which tends to favor crack growth, and surface tension, which acts to heal flaws which initiate fractures (Yakobson and Shchukin, 1993). Modeling provides an opportunity to evaluate the balance between these competing effects for geothermal reservoir conditions. In this study, we focus on the chemical environmental variables that affect fracturing via dissolution-like processes.

Chemical and environmental effects on fracture propagation in rocks and minerals – The potential of geochemical effects to influence mechanical properties under geothermal conditions has not been investigated, but this possibility is supported by related prior work. A kinetic model successfully links physical and chemical controls on subcritical crack growth of quartz based on the assumption that dissolution and fracture growth are governed by similar reaction pathways (Dove, 1995). Measurements of crack propagation velocities in minerals and rocks indicate that slow crack growth is strongly dependent on pH and temperature under laboratory conditions (Atkinson and Meredith, 1987). Laboratory hydrofractuing experiments at room temperature demonstrate that chemical additives affect the fracture number and style (Dunning and Huf, 1983). Laboratory deformation experiments indicate that rock is weaker under simulated reservoir conditions (Holl, et al., 1997). The strength of typical granitic basement rocks is reduced (relative to dry rock) by ~30% when samples are tested in contact with water at 300 °C.

Approach to coupling geochemical simulators to crack growth model – Our approach to this problem is schematically shown in Figure 1. The mineralogical and fluid properties of a reservoir are input into a geochemical modeling simulator, along with potential reactant (fluid or slurry) properties and prediction of the changes in the pore fluid chemistry is made. The geochemical simulation uses thermodynamic and kinetic data to calculate variation in fluid chemistry with time following a proposed chemical treatment. Coupling the output from the geochemical simulation with constitutive laws that relate rock properties to fluid properties will allow an assessment of the chemical treatment. In this study, we address only chemical issues (no transport is considered), and focus on the expected behavior of one mineral, quartz.

Example Calculation: Predicting the Effect of Bore-Hole Chemical Treatments On Fracture Propagation in Quartz

Experiments on whole rocks, single crystals, and glasses have shown that fluid chemistry can significantly affect material strength and fracture propagation rates. The effect of chemistry on fracture growth has been related to the surface chemistry of the mineral/fluid interface via its effect on the ease of bond breakage or its effect on the mineral/fluid interfacial tension. Although extant experimental data is insufficient to address surface tension effects on fracture propagation in minerals, there are enough data to begin to develop constitutive models that address the relationship between solution chemistry, surface chemistry, and fracture propagation in silica glasses and quartz.

Silica polymorphs, e.g., quartz, chalcedony, etc are ubiquitous cementing agents and fracture filling minerals, hence, understanding the chemical controls on fracture propagation in these minerals is a necessary starting point for understanding the limits of this approach. Dove (1994)

has shown, by correlating a large amount of experimental data, that the kinetics of dissolution of quartz can be empirically related to its surface chemical composition, in particular, the proportion of surface sites that are protonated and deprotonated. An empiric relationship was developed to explain dissolution kinetics to 300 °C for fluids with pH's ranging between 2 and 12, and sodium concentrations to 0.5 molar. Dove (1995) extended this constitutive relationship to fracture propagation in quartz, and showed for a very limited number of data sets, that a constitutive law, related to the dissolution kinetic law, could adequately explain the temperature and solution pH effects on subcritical fracture propagation. That is, higher pH's and temperatures increase the rate of subcritical fracture growth in quartz. The empiric constitutive relationship of Dove was able to reproduce the relationship beteween fracture propagation velocity and stress intensity factors for quartz in contact with deionized water for temperatures up to 80 °C, although Dove argues that the relationship should potentially be valid to 300 °C if the reaction mechanisms of subcritical crack growth and dissolution are similar. We use Dove's constitutive relationship (Dove, 1995; eq. 19, pg. 355) to assess the degree to which the fracture properties of quartz could be changed in a geothermal reservoir in response to changes in pore-fluid composition effected by bore-hole chemical treatments.

Dove's constitutive model relates fracture propagation in the subcritical crack growth region to fluid chemistry and hence, mineral surface chemistry. Dove's constitutive relationship is:

$$V_{sc} = f(K_I, T, \theta_{H2O}, \theta_{OH}) ,$$

where, V_{sc} is the velocity of subcritical crack growth, K_I is the stress intensity factor, T is the temperature, and θ_{H2O} and θ_{OH} are the fraction of quartz surface sites that are susceptible to attack by water and OH, respectively. θ_{H2O} and θ_{OH} are in turn, functions of pH (at temperature) and fluid composition (e.g., Na concentration). Dove (1994) has tabulated θ_{H2O} and θ_{OH} for various Na concentrations and pH's.

Hence, to use the relationship derived by Dove to predict fracture propagation in quartz, the *in-situ* pH and fluid composition is required. The chemical reaction simulator (React v 3.1.2; (Bethke, 1998)) and the LLNL thermodynamic equilibrium data base (Johnson and Lundeen, 1994), and dissolution kinetic data from the literature, allows the calculation of mineral/fluid equilibria to 300 °C, and thus, the *in-situ* pH and composition of the fluid.

As an example, we take a hypothetical geothermal rock with a composition similar to granite (Table 1), and use the simulator to calculate the equilibrium pore fluid at 220 °C (Table 2). Although a calculated pore fluid is used for this example, in practice the analyzed pore fluid and mineralogy would normally be used to assess the effect of a given chemical treatment. The simulator is then used to assess the changes in pore fluid composition that would occur based on addition of a well-bore chemical treatment at the surface.

At extremely high temperatures, chemical equilibrium between solid and fluid would be expected to be rapid, hence the efficacy of a one-time treatment might be short lived due to reaction of the fluid with the rock. Hence, the kinetics of reaction will determine the effective treatment time. We show in Figure 2 the effect of three chemical pH-affecting 'treatments' on the pore-fluid pH over a 10-day period following the treatment. For all three treatment scenarios we assume that 2.5 kg of rock is in contact with 1 kg of pore fluid and that the reactant is added

to the rock/fluid mixture over a 2.4 hour period. Note that at this temperature, the neutral pH of water is about 5.6.

The addition of acid results in a rather short-lived (2 days) low-pH excursion. Higher temperatures and/or larger rock/fluid ratios would be expected to decrease the time of this excursion further. In this scenario, the pH returns to the starting value after 2.5 days, hence fracture properties affected by pH only might be expected to return to ambient conditions. However, the solution composition (not shown) is also changed in other ways e.g, dissolved Si is lowered as a result of the treatment.

In contrast to acid treatment, the addition of base results in pH excursions that remain 10 days following treatment. Fluid compositions differ significantly from acid treatment, as well as differing for the two basic treatments. For example, the effect of NaOH treatment is to significantly increased dissolved Si, but the $Ca(OH)_2$ treatment is predicted to only moderately raise dissolved Si. Hence, it may be possible to tailor a well-bore treatment to obtain the a given pH regime, but moderate other fluid changes.

Predicted variation in crack growth velocity based on Dove's constitutive model – Figures 3 and 4 show the relationship between the predicted subcritical crack growth velocity and pH at reservoir conditions. For the scenario considered (220 °C), there is a two to three-fold increase in crack velocity for the base treatments, and ~2 order of magnitude decrease in crack velocity for acid treatment for a stress intensity factor of 5×10^5 N m$^{-3/2}$. As expected, at large K_I's the effect of chemical treatment is diminished (Figure 4), because the internal, rather than surficial, properties of quartz control crack propagation. Above the critical stress intensity, K_c, fracture growth is not affected by chemistry (Atkinson, 1984).

Discussion and Conclusions

The coupled geochemical-mechanical model described above suggests that slow crack growth in quartz may be active and important process in geothermal environments. Slow crack growth for a representative values of stress intensity factor depends strongly on pH, and the velocity is strongly dependent on temperature. The model is based on the kinetic relationship for crack growth in quartz proposed by Dove (1995), which assumes that dissolution and subcritical crack growth are controlled by similar reaction pathways. More sophisticated and experimentally validated models extending the concepts demonstrated in this preliminary model might find broad application for predicting coupled chemical and mechanical processes as discussed below.

Geochemical manipulation of mechanical integrity could lead to improved drilling methods and the possibility of modifying hydrofracturing or explosive/propellant fracturing to generate intersections with existing fractures caused by the regional stress field. Borehole stability might be improved by acidifying formation fluid by injection, although model results indicate that this effect is temporary. Slow crack growth might be exploited to activate movement along existing fractures loaded near the critical shear stress for slip. Fractures oriented properly with respect to the tectonic stress field can control permeability (Barton, et al., 1997). In this scenario, chemically active fluid would weaken asperities holding the fracture in place. Small displacements can dramatically increase fracture permeability. In laboratory experiments, an offset of ~ 0.5 millimeter increases fracture permeability (relative to the mated, closed fracture)

by orders of magnitude, as shown in Figure 4 (Durham and Bonner, 1994). The difference persists to pressures equivalent to depths of ~3-4 km. Minor improvements in fracture propping, whether caused by chemical weakening or other means, can dramatically affect fluid circulation in fractures.

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Table 1. Mineral composition of rock used in simulation

Mineral	Volume Percent
Quartz	30
Albite	26
Anorthite	5
K-feldspar	34
Phlogopite	4
Muscovite	1

Table 2. Composition of fluid in equilibrium with mineral assemblage shown in Table 1 at 220 °C.

Component	Concentration, M
Na	1×10^{-1}
K	4.9×10^{-3}
Ca	1.5×10^{-5}
Mg	5.4×10^{-8}
Al	1×10^{-5}
Si	4.3e-3
Cl	1.0×10^{-1}
pH	6.9
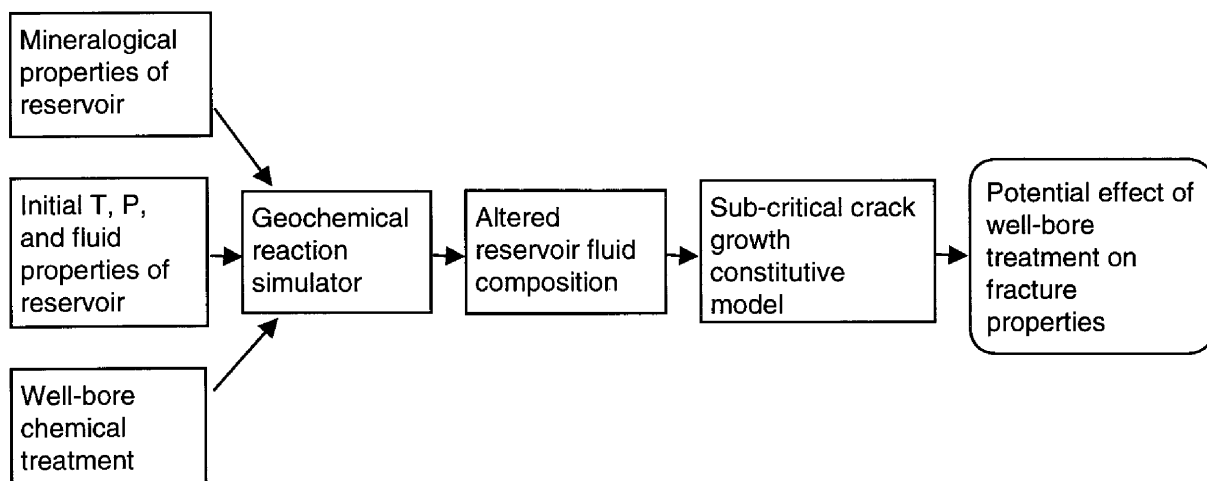
Figure 1. Schematic block diagram showing approach used to assess chemical effects on fracture propagation.
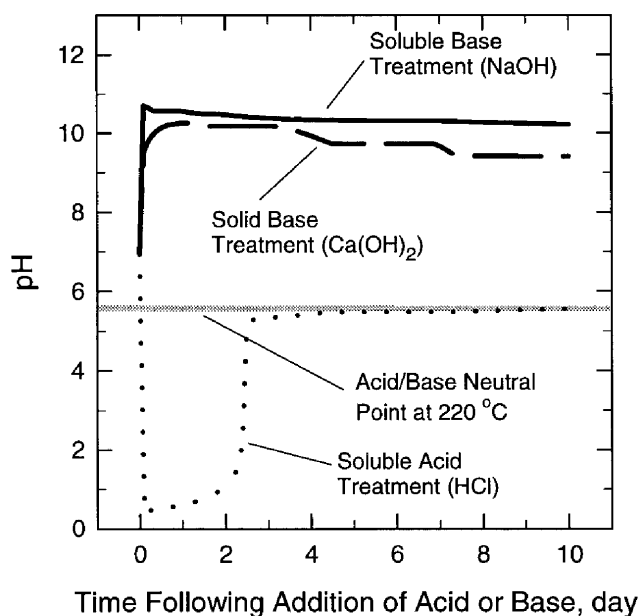

Figure 2. Predicted variation of pH with time based on results of geochemical modeling simulation of the reaction of 2.5 kg of rock with a composition similar to granite, 1 kg of pore water, and either NaOH (1 mole), Ca(OH)2 (2 moles), or HCl (1 mole). Dissolution kinetics for quartz, feldspars, and micas are explicitly accounted for in the simulation.
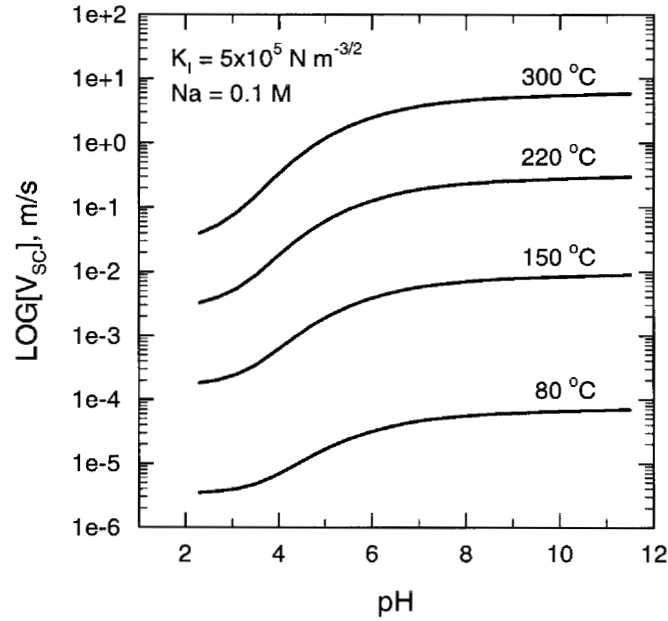
Figure 3. The relationship between the logarithm of the subcritical fracture velocity (V_{sc}) for quartz vs. pH at a stress intensity (K_I) of 5x 10^5 N m$^{-3/2}$ calculated using equation 19 in Dove (1995) for a range of temperatures.
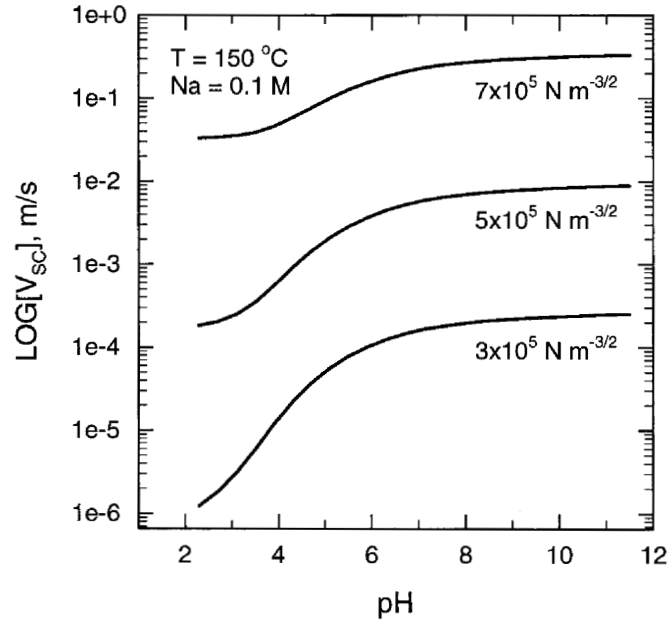

Figure 4. The relationship between the logarithm of the subcritical fracture velocity (V_{sc}) for quartz vs. pH at 150 °C for stress intensity (K_I) varying between of 3 x 10^5 and 7 x 10^5 N m$^{-3/2}$ calculated using equation 19 in Dove (1995).
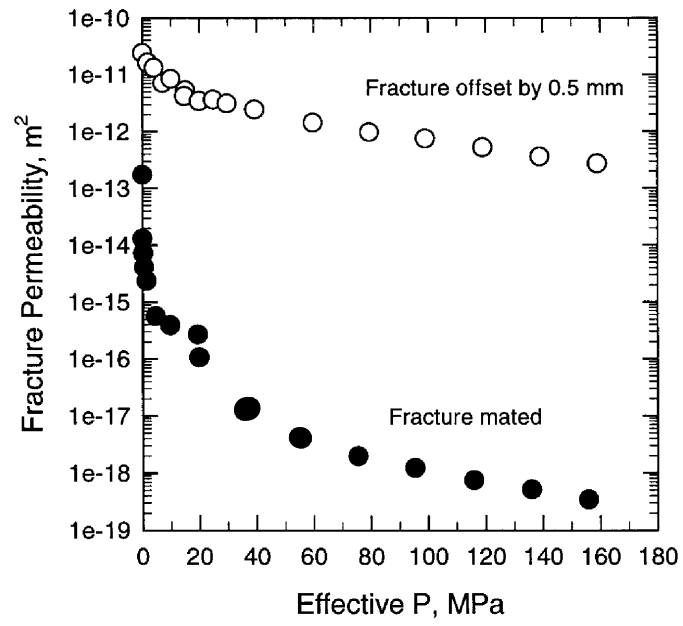
Figure 5. Variation in fracture permeability with applied pressure for offset and matched laboratory created fractures in Westerly granite (after Durham and Bonner, 1994).